The "Substitute Specification and Abstract" submitted herewith contains no new matter. In order that the examiner can satisfy himself in this regard, also submitted herewith is a copy of the original specification and abstract, from which the "Substitute Specification and Abstract" was typed.
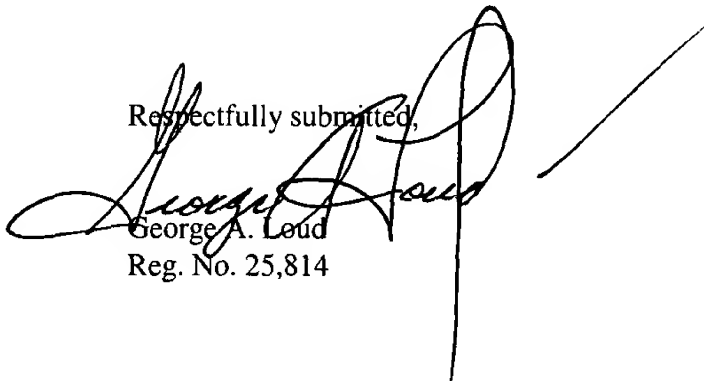
The rejection of claims 1-8 and 13 for obviousness over Vines et al taken with Kapoor is respectfully traversed. As the examiner notes, Kapoor teaches the formation of a porous insulating layer having a low dielectric constant from a "composite layer" of two or more materials one of which "can be converted to a gaseous product and at least one of which materials will remain after the conversion process as a porous matrix comprising the low dielectric constant insulation material," quoting from column 3, lines 1-8 of Kapoor. As Kapoor recognizes at column 1, lines 44-48, the presence of gaseous containing pores in the insulation material reduces the overall dielectric constant of the insulation material and, accordingly, Kapoor seeks to produce a <u>porous</u> insulating material. In contradistinction, Vines et al neither teach nor suggest formation of a porous material. Moreover, porosity would be contrary to the objective of Vines et al in producing a densified dielectric layer. See, column 2, lines 35-40 cited by the examiner in the office action. Note there that Vines et al seek "densification" of the dielectric layer. Given these different, incompatible objectives, it is respectfully submitted that it would not have been *prima facie* obvious to combine the teachings of the two references in the manner adopted by the examiner.

Regarding claim 5, neither Vines et al nor Kapoor teach or suggest use of an oxygen

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oxygen plasma for annealing. In this connection note that the carbon conversion by reaction with oxygen as taught by Kapoor is "in the range of about 800° -1200°C," quoting from column 5, line 65 to column 6, line 8 of Kapoor. In contrast, the plasma annealing of the present invention may be conducted at lower temperatures, e.g., 400°C. See page 13, lines 10-13 of applicant's original specification.

In conclusion, it is respectfully requested that the examiner reconsider the rejections of record with a view toward allowance of the pending claims.

Respectfully submitted,

George A. Loud
Reg. No. 25,814

Dated: June 4, 2002

LORUSSO & LOUD
3137 Mount Vernon Avenue
Alexandria, VA 22305

(703) 739-9393

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Please rewrite claims 1, 5, 6 and 7 as follows:

1. A method for forming an interlayer insulating film comprising the steps of:

forming a film containing [B (]boron[)], [C (]carbon[)] and H_2O on a substrate [(]by plasma enhanced chemical vapor deposition using a source gas containing an Si-C-O-H compound, an oxidative gas and a compound containing [B (]boron[)]; and

annealing said film, releasing [C (]carbon[)] and H_2O contained in said film from said film, and thereby <u>converting</u> [forming] said film into a porous SiO_2 film containing [B (]boron[)].

5. (Amended) A method according to claim 1, wherein said annealing is performed by <u>an</u> [O (]oxygen[)] plasma.

6. (Amended) A method according to claim 1, wherein a temperature of said substrate for said annealing is higher than the temperature for forming said film containing [B (]boron[)], [C (]carbon[)] and OH.

7. (Amended) A method according to claim 1, wherein said Si-C-O-H compound is one selected from the group consisting of compounds designated by a general formula $_{Si}(O)R)nH_{4-n}$, wherein [(]R = CH_3 or C_2H_5, and n = 1 to 3[)].

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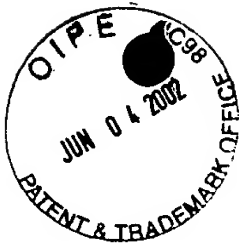
TITLE OF THE INVENTION

METHOD AND APPARATUS FOR FORMING AN INTERLAYER INSULATING FILM AND SEMICONDUCTOR DEVICE

BACKGROUND OF THE INVENTION

The present invention relates to a method for forming an interlayer insulating film and, more particularly, to a method for forming an interlayer insulating film having a low dielectric constant, which is necessary for a highly integrated semiconductor device. Progress in highly integrated semiconductor devices in recent years has resulted in a smaller spacing between wiring layers. Because reduction in the spacing between the wiring layers causes an increase in capacitance between the wiring layers, a need has been created for an interlayer insulating film having a low dielectric constant.

With recent progress in high integration of an LSI device, the wiring has been made finer and multilayered. There has also been an increase in capacitance between the wiring layers. Such an increase in capacitance has caused a great reduction in operating speed. Thus, improvement in this regard has been strongly needed. One method for reducing capacitance between the wiring layers uses an interlayer insulating film having a dielectric constant lower than that of the SiO_2

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conventionally used for an interlayer insulating film.

Typical interlayer insulating films of low dielectric constants currently under study are (1) SiOF films, and (2) organic insulating films.

(1) <u>SiOF Film</u>

A SiOF film is formed by using a source gas containing F and substituting Si-F bonds for a portion of the Si-O bonds in SiO_2. This SiOF film has a relative dielectric constant which is monotonically reduced as concentration of F in the film increases.

For forming such SiOF films, several methods have been reported (see p.82 of the monthly periodical "Semiconductor World", February issue of 1996). Most promising among these methods is one using SiH_4, O_2, Ar and SiF_4 as source gases in a high-density plasma enhanced CVD method (HDPCVD method). The relative dielectric constant of an SiOF film formed by this method is in a range of 3.1 to 4.0 (varies depending on F concentration in the film). This value is lower than the relative dielectric constant 4.0 of SiO_2, which has conventionally been used for the interlayer insulating film.

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(2) Organic Insulating Film of Low Dielectric Constant

Insulating films which have a lower dielectric constant (3.0 or lower) than a SiOF film

are organic insulating films. Table 1 shows a few organic insulating films of low dielectric

constants, which have been reported, and their respective relative dielectric constants and thermal

decomposition temperatures.

TABLE 1

Organic Insulating Film	Relative Dielectric Constant	Thermal Decomposition Temperature (°C)	Note
Fluorine-containing resin	2.4	420	p. 82 of monthly periodical "Semiconductor World", February issue of 1997
Cytop	2.1	400	p. 90 of monthly periodical "Semiconductor World", February issue of 1996
Amorphous telon	1.9	400	p. 91 of monthly periodical "Semiconductor World", February issue of 1996

However, the SiOF film has the disadvantage that an increase in concentration of F in the

film leads to a reduction in moisture absorption resistance. The reduced moisture absorption

resistance poses a serious problem, because the transistor characteristic and adhesion to an upper

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barrier metal layer are adversely affected.

Peeling-off of the organic insulating film of a low dielectric constant easily occurs, because of poor adhesion to a silicon wafer or SiO_2 film. Furthermore, the organic insulating film has the disadvantage that its heat resistivity is low. Its thermal decomposition temperature is around 400°C. The disadvantage of low heat resistivity poses a problem for annealing a wafer at a high temperature.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for forming an interlayer insulating film having good moisture absorption resistance, good heat resistivity and a low dielectric constant, a semiconductor device using the interlayer insulating film, and a semiconductor manufacturing apparatus for forming the interlayer insulating film.

According to the method for forming the interlayer insulating film according to the present invention, as illustrated in FIG. 10, the film is formed on a substrate by plasma enhanced chemical vapor deposition using a source gas (or a reaction gas) containing a Si-C-O-H compound, O_2 and B_2H_6. B (boron), C (carbon) and H_2O are contained in the film thus formed. The inventor found that when this film is annealed using an O (oxygen) plasma, C (carbon) and H_2O in the film are released from the film and thus many voids are created in the film, as illustrated in FIG. 1D. Thus, a porous SiO_2 film containing B (boron) can be formed on the

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substrate. When the film containing B (boron), C (carbon) and H_2O is formed on the substrate, H_2O contained in the film may enter into the substrate. This can be prevented in the following manner. That is, as illustrated in FIGS. 1B and 2B, an underlying insulating film is formed on the substrate, and then the film containing B (boron), C (carbon) and H_2O is formed.

Moreover, the inventor found that when a film containing a C-O-H polymer is formed by plasma enhanced chemical vapor deposition using a source gas containing Si-C-O-H compound and H_2 (hydrogen) and this film is then annealed using the O (oxygen) plasma, a porous SiO_2 film can be formed in the same manner as described above. In this case, the C-O-H polymer contained in the film is oxidized by the O (oxygen) plasma, and thus the C-O-H polymer is released from the film, and consequently the voids are created in the film.

Furthermore, the inventor found that in forming a film containing the C-O-H polymer, if O_2 is added to the source, larger voids are created in the film, and the content of SiO_2 in the film increases and thus the film is stabilized.

Preferably, the film containing the C-O-H polymer has such a thinness that the C-O-H polymer is sufficiently oxidized by the O (oxygen) plasma. Therefore, the method of the present invention provides a porous SiO_2 film having a desired thickness by alternately repeating the formation of the film containing the C-O-H polymer and the oxidization by the O (oxygen) plasma, as illustrated in FIG. 3C.

The porous SiO_2 film formed as described above has many voids and thus has a surface area larger than the surface area of the SiO_2 film having no void. Because the porous SiO_2 film is prone to absorb moisture in the air it is subjected to H (hydrogen) plasma treatment as illustrated in FIGS. 1E, 2E, 3D and 3L. By this treatment, dangling Si-O bonds on the void surfaces are substituted with Si-H bonds. As a result, it is possible to prevent the moisture from being adsorbed on the surface of the voids. Furthermore, a cover insulating film is formed on the porous SiO_2 film as illustrated in FIGS. 1H and 2M, whereby it is possible to prevent moisture from being absorbed.

The semiconductor manufacturing apparatus according to the present invention has control means for controlling flow rate control means which, in turn, controls the flow rate of the source gas, and switching means for switching a high-frequency voltage applied to a chamber, as illustrated in FIG. 6.

The control means allows alternately repeating the plasma enhanced chemical vapor deposition and the annealing in one chamber, as illustrated in FIG. 4. That is, during a time period from T1 to T2 in FIG. 4, the source gases (H_2, TEOS (Tetra-Ethyl-Ortho-Silicate) and Ar) are introduced into the chamber and the high-frequency voltage is applied to the chamber, whereby plasma enhanced chemical vapor deposition takes place. During the time period from T2 to T3, O_2 is applied to the chamber, without the high-frequency voltage, whereby the annealing is performed in an atmosphere of O_2.

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Furthermore, as illustrated in FIG. 5, this control means allows plasma enhanced chemical vapor deposition and annealing in a plasma atmosphere to be alternately repeated in one chamber. That is, during the time period from T1 to T2 in FIG. 5, the source gases (H_2, TEOS, O_2 and Ar) are introduced into the chamber and the high-frequency voltage is applied to the chamber, whereby the plasma enhanced chemical vapor deposition takes place. During the time period from T2 to T3, O_2 alone is introduced into the chamber which the high-frequency voltage is applied to, whereby the annealing is performed in the plasma atmosphere of O_2.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A to 1H are cross-sectional views showing a method for forming an interlayer insulating film according to a first embodiment of the present invention;

FIGS. 2A to 2M are cross-sectional views showing the method for forming the interlayer insulating film according to a second embodiment of the present invention;

FIGS. 3A to 3L are cross-sectional views showing the method for forming the interlayer insulating film according to third and fourth embodiments of the present invention;

FIG. 4 shows characteristics of time dependency of an Ar flow rate, a TEOS flow rate, an H_2 flow rate, an O_2 flow rate and plasma in the method for forming the interlayer insulating film according to the third embodiment of the present invention and a semiconductor manufacturing apparatus;

FIG. 5 shows the characteristics of the time dependency of the Ar flow rate, the TEOS flow rate, the H_2 flow rate, the O_2 flow rate and the plasma in the method for forming the

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interlayer insulating film according to the fourth embodiment of the present invention and the

semiconductor manufacturing apparatus; and

FIG. 6 shows a semiconductor manufacturing apparatus according to an embodiment of

the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments of the present invention will now be described with reference to

the accompanying drawings.

(a) First Embodiment of the Method

Referring to FIGS. 1A to 1H, first, as shown in FIG. IA, a BPSG (borophosphosilicate

glass) film 102 is formed on a silicon substrate 101. Then, an aluminum film is formed on the

BPSG film 102 and then the aluminum film is patterned, whereby an aluminum wiring layer 103

is formed. A substrate 104 comprises the silicon substrate 101, the BPSG film 102 and the

aluminum wiring layer 103 which are formed in the foregoing manner.

Then, as shown in FIG. 1B, a SiO_2 film 105 (an underlying insulating film) is formed on

the substrate 104. This SiC)$_2$ film 105 is formed by a PECVD method (plasma enhanced

chemical vapor deposition). SiH_4 and N_2O are used as a source gas. The thickness of the SiO_2

film 105 is 100 nm.

Then, as shown in FIG. 1C, a SiO_2 film 106 having a thickness of 500 nm and containing B (boron) is formed on the SiO_2 film 105 (the underlying insulating film). The SiO_2 film 106 containing B (boron) is formed by a CVD method (Enhanced chemical vapor deposition) under a pressure of 1 Torr by applying RF power having a frequency of 13.56 MHz with the silicon substrate 101 kept at 100°C in an atmosphere of TEOS (Tetra-Ethyl-Ortho-Silicate), B_2H_6, O_2 and Ar. C (carbon) and an OH group as well as B are contained in the B-(boron)-containing SiO_2 film 106 formed in this manner. In this case, the flow rates of the source gases are as follows: the flow rate of TEOS is 30 sccm, the flow rate of B_2H_6 is 30 sccm, the flow rate of O_2 is 90 sccm, and the flow rate of Ar is 900 sccm.

Then, as shown in FIG. 1D, the SiO_2 film 106 containing B (boron) is subjected to O (oxygen) plasma treatment. At this time, C (carbon) and the OH groups contained in the SiO_2 film 106 containing B (boron) react with O atoms in O (oxygen) plasma. Thus, C (carbon) and the OH groups are changed to CO_2 and H_2O, and then CO_2 and H_2O are released from the film thereby creating voids at sites which have contained C (carbon) and the OH groups in the SiO_2 film 106 containing B (boron) and consequently, changing the SiO_2 film 106 containing B (boron) to a porous SiO_2 film 107 containing B (boron).

Subsequently, as shown in FIG. 1E, the porous SiO_2 film 107 containing B (boron) is subjected to H (hydrogen) plasma treatment. By this treatment, dangling Si-O bonds in the film are substituted with Si-H bonds. Thus, the film is improved in moisture absorption resistance.

Then, as shown in FIG. 1F, an SiO_2 film 108 is formed on the porous SiO_2 film 107 containing B (boron). This SiO_2 film 108 is formed in order to planarize the surface. The SiO_2 film 108 is formed by the CVD method using TEOS and O_3 as the source gas. The O_3 has sufficient density to oxidize TEOS. Thus, the SiO_2 film 108 is a fluidized SiO_2 film.

Then, as shown in FIG. 1G, the SiO_2 film 108 is etched, whereby the surface is planarized. At this time, the SiO_2 film (the underlying insulating film) 105 and the porous SiO_2 film 107 containing B (boron), which are previously formed, are partly removed by etching. The planarizing by the etching is limited so that the SiO_2 film 105 formed on a convexity 103a of the aluminum wiring layer is not completely removed.

Then, as shown in FIG. 1H, a SiO_2 film (a cover insulating film) 109 is formed on the planarized surface. This SiO_2 film 109 is formed by the PECVD method. SiH_4 and N_2O are used as the source gas. The thickness of the SiO_2 film 109 is 100 nm.

The interlayer insulating film having good heat resistivity, good moisture absorption resistance and a low dielectric constant is formed on the substrate 104 by the SiO_2 film (the underlying insulating film) 105, the SiO_2 film 108, the SiO_2 film (the cover insulating film) 109 and the porous SiO_2 film 107 containing B (boron) which are formed as described above. That is, the SiO_2 film 107 containing B (boron) is porous, and thus the dielectric constant of the SiO_2 film 107 is 2.0 to 3.0. This dielectric constant is lower than the dielectric constant 4.0 of a typical nonporous SiO_2 film. Moreover, the typical SiO_2 film 109 is formed on the porous SiO_2 film 107

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containing B (boron). Thus, it is possible to prevent moisture from penetrating into the SiO_2 film 107 containing B (boron). Furthermore, the heat resistivity of the SiO_2 film 105, 108, 109 and the porous SiO_2 film 107 containing B (boron) is better than the heat resistivity of an organic insulating film.

Though TEOS (Tetra-Ethyl-Ortho-Silicate) is used as the Si-C-O-H ccnipound in the above embodiment, Tri-methoxy-silane ($Si(OCH_3)_3H$) or the like may be used. That is, any compound of the general formula $Si(OR)nH_{4-n}$ ($R=CH_3$ or C_2H_5, n=1 to 3) may be used as the Si-C-O-H compound. This is also true in the following embodiments.

(b) Second Embodiment

The second embodiment applies the first embodiment to a damascene process.

Referring to FIGS. 2A to 2M, first as shown in FIG. 2A, a BPSG (borophosphosilicate glass) film 202 is formed on a silicon substrate 201. An aluminum layer is formed on the BPSG film 202 and then the aluminum layer is patterned, whereby an aluminum wiring layer 203 is formed. A substrate 204 comprises the silicon substrate 201, the BPSG film 202 and the aluminum wiring layer 203.

Then, as shown in FIG. 2B, a SiO_2 film (the underlying insulating film) 205 having a thickness of 100 nm is formed on the aluminum wiring layer 203. This SiO_2 film 205 is formed

by the PECVD method (plasma enhanced chemical vapor deposition). SiN_4 and N_2O are used as the source gas.

Then, as shown in FIG. 2C, a SiO_2 film 206 having a thickness of 500 nm and containing B (boron) is formed on the SiO_2 film (the underlying insulating film) 205. The SiO_2 film 206 containing B (boron) is formed by the CVD method (plasma enhanced chemical vapor deposition) under a pressure of 1 Torr by applying RF power at a frequency of 13.56 MHz and RF power at a frequency of 400 kHz with the silicon substrate 201 kept at 100°C in the atmosphere of TEOS (Tetra-Ethyl-Ortho-Silicate), B_2H_6, O_2 and Ar. C (carbon) and the OH group as well as B are contained in the B-(boron)-containing SiO_2 film 206 formed in this way.

Then, as shown in FIG. 2D, the SiO_2 film 206 containing B (boron) is subjected to the O (oxygen) plasma treatment after the temperature of the silicon substrate 201 is raised to 400°C. At this time, C (carbon) and the OH groups contained in the SiO_2 film 206 containing B (boron) react with the O atoms in the O (oxygen) plasma. Thus, C (carbon) and the OH groups are changed to CO_2 and H_2O, and then CO_2 and H_2O are released from the film thereby creating voids at the sites which have contained C (carbon) and the OH group in the SiO_2 film 206 containing B (boron). Consequently, the SiO_2 film 206 containing B (boron) is changed to a porous SiO_2 film 207 containing B (boron).

Subsequently, as shown in FIG. 2E, the porous SiO_2 film 207 containing B (boron) is subjected to the H (hydrogen) plasma treatment. By this treatmant, the dangling Si-O bonds in

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the film are substituted with Si-H bonds. Thus, the film is improved in the moisture absorption resistance.

Then, as shown in FIG. 2F, the SiO_2 film (the underlying insulating film) 205 and the porous SiO_2 film 207 containing B (boron) are patterned to form a damascene trench 208. This damascene trench 208 communicates with the aluminum wiring layer 203 formed under the SiO_2 film 205.

Then, as shown in FIG. 2G, an SiO_2 film (a first insulating film) 209 is formed on the porous SiO_2 film 207 containing B (boron) and on the sides and bottom of the damascene trench 208. This SiO_2 film 209 is formed by the PECVD method (plasma enhanced chemical vapor deposition). The SiO_2 film 209 formed on the sides of the damascene trench 208 can prevent Cu, to be later formed in the damascene trench 208, from diffusing into the porous SiO_2 film 207 containing B (boron).

Then, as shown in FIG. 2H, the SiO_2 film (the first insulating film) 209 is anisotropically etched. This results in removing the SiO_2 film 209 other than that portion on the sides of the damascene trench 208. A contact hole communicating with the aluminum wiring layer 203 is formed in the bottom of the damascene trench 208.

Subsequently, as shown in FIG. 21, a Cu-plated film 210 is formed in the damascene trench 208 and on the porous SiO_2 film 207 containing B (boron). The Cu-plated film 210

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formed in the damascene trench 208 is used as Cu wiring.

Then, as shown in FIG. 2J, the Cu-plated film 210 formed on the porous SiO_2 film 207 containing B (boron) is polished and removed by CMP (Chemical Mechanical Polishing). Thus, the Cu-plated film remains only in the damascene trench 208.

Then, as shown in FIG. 2K, a TiN film 211 for a barrier is formed on the damascene trench 208. This TiN film 211 can prevent Cu in the damascene trench 208 from diffusing into the SiO_2 film to be later formed on the damascene trench 208.

Then, as shown in FIG. 2L, the patterning leaves a Tin 10 film 211a formed on the damascene trench 208 and etches away the TiN film 211 formed on the other portions.

Subsequently, as shown in FIG. 2M, a SiO_2 film (the cover insulating film) 212 is formed on the SiO_2 film 207 containing B (boron) and the TiN film 211a. This SiO_2 film 212 is formed by the PECVD method. SiH_4 and N_2O are used as the source gas.

As described above, the interlayer insulating film having good heat resistivity, good moisture absorption resistance and a low dielectric constant is formed on the substrate 204. That is, the SiO_2 film 207 containing B (boron) is porous, and thus the dielectric constant of the SiO_2 film 207 is lower than that of a typical B-containing SiO_2 film(a BSG film). Moreover, the typical SiO_2 fiihn (the cover insulating film) 212 is formed on the porous SiO_2 film 207

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containing B (boron) to prevent the moisture from penetrating into the porous SiO_2 film 207.

Furthermore, the heat resistivity of the porous SiO_2 film 207 containing B (boron) is better than

the heat resistivity of an organic insulating film.

(c) Third Embodiment

Referring to FIGS. 3A to 3L, first, as shown in FIG. 3A, a BPSG (borophosphosilicate

glass) film 302 is formed on a silicon substrate 301. The aluminum layer is formed on the BPSG

film 302 and then the aluminum layer is patterned, whereby an aluminum wiring layer 303 is

formed. A substrate 304 comprises the silicon substrate 301, the BPSG film 302 and the

aluminum wiring layer 303.

Then, as shown in FIG. 3B, a SiO_2 film (the underlying insulating film) 305 is formed on

the aluminixn wiring layer 303. This SiO_2 film 305 is formed by the PECVD method (plasma

enhanced chemical vapor deposition). SiH_4 and N_2O are used as the source gas.

Then, as shown in FIG. 3C, a porous SiO_2 film 306 is formed on the SiO_2 film (the

underlying insulating film) 305. This porous SiO_2 film 306 is formed by using the plasma

changing with the passage of time as shown in FIG. 4 in the atmosphere of TEOS (Tetra-Ethyl-

Ortho- Silicate), with the flow rates of H_2, Ar, TEOS and O_2 also changing with the passage of

time as shown in FIG. 4 and with the silicon substrate 301 kept at 350°C. During the time

period from T1 to T2 in FIG. 4, the plasma is generated in an atmosphere of TEOS and H_2, so

that the process of the PECVD (plasna enhanced chemical vapor deposition) takes place. At this time, the pressure is 1.0 Torr. The film formed at this time contains many C-O-H polymers and has a network structure composed of a large number of SiO_2 molecules. During the time period from T2 to T3 in the drawing, the plasma is not generated, so that annealing takes place in an atmosphere of O_2. At this time, the pressure is 0.1 Torr. By this annealing, the C-O-H polymers contained in the film formed during the time period from T1 to T2 are oxidized by O_2 and then the C-O-H polymers are released from the film. Thus, only the network structure of SiO_2 remains in the film, and therefore many voids are created in the film. In order to sufficiently oxidize the C-O-H polymers, it is desirable that the thickness of the film containing the C-O-H polymers be small, which is accomplished by setting a small interval between T2 and T1.

The porous SiO_2 film 306 is formed by repeating the PECVD in the atmosphere of TEOS, H_2 and Ar and the annealing in the atmosphere of O_2 as described above.

In this embodiment, the RF power with a frequency of 13.56 MHz and the RF power with a frequency of 400 kHz are used as the RF power for generating the plasma. The respective RF powers are 300 W and 50 W. In FIG. 4, T1 = 5 sec, T2 = 10 sec and T3 = 15 sec.

Then, as shown in FIG. 3D, the porous SiO_2 film 306 is subjected to the H (hydrogen) plasma treatment. By this treatment, the dangling Si-O bonds on the inner surfaces of the voids are replaced by the Si-H bonds. Thus, the film improves in the moisture absorption resistance.

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Subsequently, as shown in FIG. 3E, the SiO_2 film (the underlying insulating film) 305 and the porous SiO_2 film 306 are opened by patterning, whereby a damascene trench 307 is formed. This damascene trench 307 reaches to the aluminum wiring layer 303 formed under the SiO_2 film 305.

Then, as shown in FIG. 3F, a TiN film 308, serving as a barrier, is formed on the porous SiO_2 film 306 and on the sides and bottom of the damascene trench 307. This TiN film 308 can prevent the Cu-plated film, to be later formed in the damascene trench 307, from diffusing around the damascene trench 307.

Then, as shown in FIG. 3G. a Cu seed layer 309 is formed on the TiN film 308. This Cu seed layer 309 is used as a conductive layer for supplying a current to form the Cu-plated film on the Cu seed layer 309.

Then, as shown in FIG. 3H, a Cu-plated film 310 is formed on the Cu seed layer 309, and Cu is buried in the damascene trench 307.

Subsequently, as shown in FIG. 3I, the TiN film 308 formed on the porous SiO_2 film 306, the Cu seed layer 309 and the Cu-plated film 310 are polished and rezinved by the CMP method (Chemical Mechanical Polishing method). Thus, the Cu-plated film remains only in the damascene trench 307.

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Then, as shown in FIG. 3J, an SiN film 311 for preventing Cu from oxidizing is formed

on the Cu-plated film 310 polished by the CMP method. Desirably, an anti-oxidizing film such

as the SiN film is formed as soon as possible after the polishing by the CMP method, because Cu

is prone to be oxidized compared to Al.

Then, as shown in FIG. 3K, a porous SiO_2 film 312 is formed on the SiN film 311. This

porous SiO_2 film 312 is formed in the same manner as the porous SiO_2 film 306 previously

formed. That is, the porous SiO_2 film 312 is formed by using the plasma changing with the

passage of time as shown in FIG. 4 wherein the flow rates of TEOS, H_2, Ar and O_2 change with

passage of time as shown in FIG. 4 with the silicon substrate 301 kept at 350°C. The RF power

with a frequency of 13.56 MHz and the RF power with a frequency of 400 kHz are used as the

RF power for use in this case. The respective powers are 300 W and 50 W. In FIG. 4, T1= 5 sec,

T2 = 10 sec and T3 = 15 sec.

Then, as shown in FIG. 3L, the porous SiO_2 film 312 is subjected to the H (hydrogen)

plasma treatment. By this treatment, the dangling Si-O bonds on the inner surfaces of the voids

are replaced by the Si-H bonds. Thus, the moisture absorption resistance of the film is improved.

As described above, the interlayer insulating film having good heat resistivity, good

moisture absorption resistance and a low dielectric constant is formed on the substrate 304. That

is, the SiO_2 films 306 and 312 are porous, and thus the dielectric constant of these films is 2.0 to

3.0. This dielectric constant is lower than the dielectric constant of the typical nonporous SiO_2

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film. Moreover, the porous SiO_2 films 306 and 312 are subjected to the H (hydrogen) plasma treatment. Thus, the moisture absorption resistance of the films is improved. Additionally, the heat resistivity of the porous SiO_2 films 306 and 312 is better than the heat resistivity of the organic insulating films.

(d) Fourth Embodiment

The fourth embodiment differs from the third embodiment only in the method for forming the porous SiO_2 film. First, as shown in FIG. 3A, the BPSG 20 (borophosphosilicate glass) film 302 is formed on the silicon substrate 301. The aluminum layer is formed on the BPSG film 302 and then the aluminum layer is patterned, whereby the aluminum wiring layer 303 is formed. The substrate 304 canprises the silicon substrate 301, the BPSG film 302 and the aluminum wiring layer 303.

Then, as shown in FIG. 3B, the SiO_2 film 305 (the underlying insulating film) is formed on the aluminum wiring layer 303. This SiO_2 film 305 is formed by the PECVD method (plasma enhanced chemical vapor deposition). SiH_4 and N_2O are used as the source gas.

Then, as shown in FIG. 3C, the porous SiO_2 film 306 is formed on the SiO_2 film (the underlying insulating film) 305. This porous SiO_2 film 306 is formed by using the plasmas with the flow rates changing with the passage of time as shown in FIG. 5, with the silicon substrate 301 kept at 350°C.

The fourth embodiment differs from the third embodimeni in that the plasma does not change with the passage of time and thus a plasma having a fixed intensity is generated during film formation and in that O_2 is added to the atmosphere of TEOS, H_2 and Ar during the film formation.

During the time period from T1 to T2 in FIG. 5, the plasma CVD (plasma enhanced chemical vapor deposition) takes place in the atmosphere of TEOS, H_2, Ar and O_2. At this time, the pressure is 1.0 Torr. Many C-O-H polymers are contained in the film formed at this time. Because of O_2 added to the atmosphere, the content of SiO_2 in the film is higher than the content of SiO_2 of the third embodiment. Thus, the film is improved in stability. Decomposition reaction of OH allows the larger network structure of SiO_2 to be formed.

Moreover, during the time period from T2 to T3 in FIG. 5, the annealing takes place in an atmosphere of O_2 plasma. At this time, the pressure is 0.1 Torr. When the annealing occurs in the O_2 plasma in this manner, outgassing from the film improves compared to the outgassing by annealing in the O_2 atmosphere in the third embodiment. By this annealing, the C-O-H polymers contained in the film formed during the time period from T1 to T2 are oxidized by O_2, and then the C-O-H polymers are released from the film. Thus, only the network structure of SiO_2 remains in the film, and many voids are created in the film. The size of the void created in this fourth embodiment is larger than the size of the void of the third embodiment. In order to sufficiently oxidize the C-O-H polymers, it is desirable that the thickness of the film containing the C-O-H polymers be sufficiently small due to a short interval between T2 and T1.

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The porous SiO_2 film 306 is formed by repeating the plasma CVD in the atmosphere of TEOS, H_2, Ar and O_2 and the annealing in the O_2 plasma as described above.

In this embodiment, the RF power with a frequency of 13.56 MHz and the RF power with a frequency of 400 kHz are used in order to generate the plasma. The respective RF powers are 300W and 50W. In FIG. 5, T1= 5 sec, T2= 10 sec and T3 = 15 sec.

Then, as shown in FIG. 3D, the porous SiO_2 film 306 is subjected to the H (hydrogen) plasma treatment. By this treatment, the dangling Si-O bonds on the inner surfaces of the voids are replaced by the Si-H bonds. Thus, the film is improved in moisture absorption resistance.

Subsequently, as shown in FIG. 3E, a damascene trench 307 is formed in the SiO_2 film 305 (the underlying insulating film) and the porous SiO_2 film 306. This damascene trench 307 communicates with the aluminum wiring layer 303 formed under the SiO_2 film 305.

Then, as shown in FIG. 3F, the TiN film 308 for the barrier metal is formed on the porous SiO_2 film 306 and on the sides and the bottom of the damascene trench 307. This TiN film 308 prevents the Cu-plated film subsequently formed in the damascene trench 307 from diffusing from the damascene trench 307.

Then, as shown in FIG. 3G. the Cu seed layer 309 is formed on the TiN film 308. This Cu seed layer 309 is used as the conductive layer for supplying the current to form the Cu-plated

film on the Cu seed layer 309.

Then, as shown in FIG. 3H, the Cu-plated film 310 is formed on the Cu seed layer 309, and the damascene trench 307 is filled with Cu.

Subsequently, as shown in FIG. 3I, the TiN film 30E formed on the porous SiO_2 film 306, the Cu seed layer 309 and the Cu-plated film 310 are polished and removed by the CMP method (Chemical Mochanical Polishing method). Thus, the Cu-plated film remains only in the damascene trench 307.

Then, as shown in FIG. 3J, a SiN film 311 for preventing Cu from oxidizing is formed on the Cu-plated film 310 polished by the CMP method. Preferably, the anti-oxidizing film such as the SiN film is formed as soon as possible after the polishing by the CMP method, because Cu is more prone to be oxidized than Al.

Then, as shown in FIG. 3K, the porous SiO_2 film 312 is formed on the SiN film 311. This porous SiO_2 film 312 is formed in the same manner as the porous SiO_2 film 306 previously described. That is, the porous SiO_2 film 312 is formed by using a pulsed plasma as shown in FIG. 5 in an atmosphere of TEOS, H_2, Ar and O_2, having flow rates changing with time as also shown in FIG. 5, with the silicon substrate 301 kept at 350°C. The RF power with a frequency of 13.56 MHz and the RF power with a frequency of 400 kHz are used as the RF power in this embodiment. The respective RF powers are 300 W and 50 W. In FIG. 5, T1 = 5 sec, T2 = 10

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sec and T3 = 15 sec.

Then, as shown in FIG. 3L, the porous SiO_2 film 312 subjected to the H (hydrogen) plasma treatment. By this treatment, the dangling Si-O bonds on the inner surfaces of the voids are replaced by Si-H bonds. The film is thus improved in moisture absorption resistance.

As described above, the interlayer insulating film having good heat resistivity, good moisture absorption resistance and low dielectric constant is formed on the substrate 304. That is, the size of the voids in the porous SiO_2 films 306 and 312 is larger the size of the voids of the third embodiment. Thus, the dielectric constant of the porous SiO_2 films 306 and 312 is 2.0 to 2.5. This dielectric constant is even lower than the dielectric constant of the third embodiment. The porous SiO_2 films 306 and 312 are subjected to the H (hydrogen) plasma treatment to improve the moisture absorption resistance of the film. Furthermore, the heat resistivity of the porous SiO_2 films 306 and 312 is better than the heat resistivity of the organic insulating films.

Although, the annealing methods according to the third and fourth embodiments are applied to an interlayer insulating film not containing B, they may also be applied to the interlayer insulating films 106, 206 containing B in the first and second embodiments. Conversely, the annealing methods according to the first and second embodiments may be applied to the interlayer insulating film not containing B in the third and fourth embodiments.

(2) Description of an Apparatus for Forming the Interlayer Insulating Film

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According to the Present Invention

The apparatus for forming the interlayer insulating film will now be described with reference to FIGS. 4, 5 and 6.

FIG. 6 shows the basic structure of an apparatus for forming the interlayer insulating film as including chamber 512 for forming the film, a gas inlet 510 for introducing the reaction gas into the chamber, a wafer 515, a gas discharging device 511 for uniformly dispersing the source gas onto the wafer 515, a wafer holder 513 containing a heater and a gas outlet 514 for exhausting the source gas from the chamber.

A pipe 509 is connected to the gas inlet 510 and branch pipes 517, 518, 519 and 520 are connected to an upstream portion of the pipe 509. The branch pipe 517 is used to supply Ar (argon) and the branch pipe 518 is used to supply H_2 (hydrogen). An ozone generator 506 is connected to the branch pipe 519. O_2 introduced from the upstream is partly changed to O_3, and thus a mixed gas of O_2 and O_3 is introduced into the pipe 509. A container 507 containing TEOS (Tetra-Ethyl-C)rtho-Silicate) is connected to the branch pipe 520. Ar or He containing TEOS is introduced into the pipe 520 by bubbling of Ar or He through the TEOS. The pipes 509 and 520 are heated by a heater 527 so that TEOS in the pipe is not liquefied. Numeral 508 denotes the heater for heating TEOS. Additionally, MFC (a flow rate controller) is provided in each of these branch pipes. Control signals 521, 522, 523 and 524 are output from control means 501 to the MFCs. The reaction gas is controlled by these control signals so that the reaction gas is supplied at a desired flow rate.

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A high-frequency power generator 516 supplies RF power at a frequency of 13.56 MHz

to the discharging device 511. A high-frequency voltage generator 530 supplies the RF power at

a frequency of 400 kHz to the wafer holder 513, and switching means 526 and 529 route the RF

power generated by the high-frequency power generators 516 and 530 to the chamber.

Control signals 525 and 528 are output from the control means 501 to the switching

means 526 and 529, respectively, so that the tine of application of the RF power is controlled.

FIGS. 4 and 5 show the flow rates of the reaction gas and the tine of application of the HF

power which are controlled by the control means 501.

During the time period from T1 to T2 in FIG. 4, MFC 502 (for supplying Ar), MFC 503

(for supplying H_2) and MFC 505 (for supplying TEOS) are opened and MFC 504 (for supplying

O_2) is closed by the control signals 521, 522, 523 and 524. Thus, Ar, H_2 and TEOS are

introduced into the chamber. At the same tine, the switching means 526 and 529 are turned on by

the control signals 525 and 528, respectively, whereby the RF power is applied to the chamber

512. Thus, during the time period from T1 to T2, the PECVD (plasma enhances chemical vapor

deposition) takes place in the chamber in an atmosphere of Ar, H_2 and TEOS. During this time

period, the wafer is kept at 350°C by a substrate holder 513 containing a heater.

During the time period from T2 to T3 in FIG. 4, the MF'C 502 (for supplying Ar), the

MFC 503 (for supplying H_2) and the MFC 505 (for supplying TEOS) are closed and the MFC

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504 (for supplying O_2) is opened by the control signals 521, 522, 523 and 524. At the same time,

the switching means 526 and 529 are turned off by the control signals 525 and 528, respectively,

whereby no RF power is applied to the chamber 512. Thus, O_2 alone is introduced into the

chamber, so that the annealing by O_2 occurs in the chamber. During this time period, the wafer is

kept at 350°C by the substrate holder 513 containing the heater. In FIG. 4, Ti = 5 sec. T2 = 10 sec

and T3 = 15 sec.

FIG. 5 shows another example of the flow rates of the reaction gas and the time of

application of the RF power which are controlled by the control means 501. FIG. 11 differs from

FIG. 4 in the flow rate of O_2 and the time of application of the RF power.

During the time period from T1 to T2 in FIG. 5, all of the MFC 502 (for supplying Ar),

the MFC 503 (for supplying H_2), the MFC 504 (for supplying O_2) and the MFC 505 (for

supplying TEOS) are opened by the control signals 521, 522, 523 and 524. Thus, Ar, H_2, O_3 and

TEOS are introduced into the chamber. At the same dine, the switching means 526 and 529 are

turned on by the control signals 525 and 528, respectively, whereby the RF power is applied to

the chamber. Thus, during the time period from T1 to T2, the PECVD (plasma enhanced

chemical vapor deposition) takes place in the chamber in an atmosphere of Ar, H_2, O_3 and TEOS.

During this time period, the wafer is kept at 350°C by the substrate holder 513 containing the

heater.

During the time period from T2 to T3 in FIG. 5, the MFC 502 (for supplying Ar), the

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MFC 503 (for supplying H_2) and the MFC 505 (for supplying TEOS) are closed by the control signals 521, 522 and 524. The O_2 flow rate during this time period is increased by the control signal 523, over the O_2 flow rate during the time period from T1 to T2. Moreover, RF power is applied to the chamber differently than in FIG. 4. O_2 alone is introduced into the chamber, so that the annealing by O_2 occurs in an O_2 plasma. During this time period, the wafer is kept at 350°C by the substrate holder 513 with the built-in heater. In FIG. 5, Ti = 5 sec, T2 = 10 sec and T3 = 15 sec.

ABSTRACT OF THE DISCLOSURE

A method for forming an interlayer insulating film includes the steps of forming an underlying insulating film on a substrate; forming a film containing B (boron), C (carbon) and H_2O) on the underlying insulating film by plasma enhanced chemical vapor deposition using a source gas containing an Si-C-O-H compound, an oxidative gas and a compound containing B (boron); releasing C (carbon) and H_2O in the film from the film by annealing the film, and thereby forming a porous SiO_2 film containing B (boron); and subjecting to the porous SiO_2 film containing B (boron) to H (hydrogen) plasma treatment, and then forming a cover insulating film.